

Effects of Carbonyl Bond, Metal Cluster Dissociation, and Evaporation Rates on Predictions of Nanotube Production in High-Pressure Carbon Monoxide

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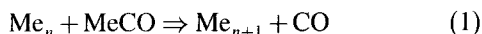
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The high-pressure carbon monoxide (HiPco) process for producing single-wall carbon nanotubes (SWNTs) uses iron pentacarbonyl as the source of iron for catalyzing the Boudouard reaction. Attempts using nickel tetracarbonyl led to no production of SWNTs. This paper discusses simulations at a constant condition of 1300 K and 30 atm in which the chemical rate equations are solved for different reaction schemes. A lumped cluster model is developed to limit the number of species in the models, yet it includes fairly large clusters. Reaction rate coefficients in these schemes are based on bond energies of iron and nickel species and on estimates of chemical rates for formation of SWNTs. SWNT growth is measured by the coformation of CO₂. It is shown that the production of CO₂ is significantly greater for FeCO because of its lower bond energy as compared with that of NiCO. It is also shown that the dissociation and evaporation rates of atoms from small metal clusters have a significant effect on CO₂ production. A high rate of evaporation leads to a smaller number of metal clusters available to catalyze the Boudouard reaction. This suggests that if CO reacts with metal clusters and removes atoms from them by forming MeCO, this has the effect of enhancing the evaporation rate and reducing SWNT production. The study also investigates some other reactions in the model that have a less dramatic influence.

Keywords: Single-Wall Carbon Nanotubes, HiPco, Nanotube Production Cluster Model.

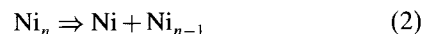
1. INTRODUCTION

In the high-pressure carbon monoxide (HiPco) process the Boudouard reaction, catalyzed by iron, produces single-wall carbon nanotubes (SWNTs).^{1,2} Whereas using iron as a catalyst yields significant amounts of SWNTs, attempts to use nickel as a catalyst have not led to SWNT production. At first, differences in the nucleation rates of iron and nickel were thought to have a significant effect on production. However, parametric studies of nucleation³ did not show a significant influence on production since there are other pathways for producing dimers and larger clusters without direct Fe + Fe nucleation. It was noted that one difference between iron and nickel is their different affinities for bonding with CO. Sunderlin et al.⁴ report the bond energy for NiCO is about 170 kJ/mol (20,468 K) and that for FeCO is about 35 kJ/mol (4214 K). The higher binding energy of NiCO will slow down its dissociation and possibly speed up its formation compared with FeCO. In the models we have included cluster growth by the exchange reaction



where the reaction rate is taken to be the gas kinetic rate (Me = metal). These reactions are less likely for nickel because the binding energy of NiCO (170 kJ/mol) is only slightly smaller than that of Ni_{n-1}Ni ($E_a = 203$ kJ/mol, $n = 2$). This is not the case for Fe_{n-1}Fe, where the FeCO bond energy E_a is 35 kJ/mol, whereas that for Fe-Fe is about two times greater, 75 kJ/mol. The reverse of these reactions is the "CO-enhanced evaporation" reactions in which CO abstracts Me from the cluster. Since the binding energy of NiCO is much stronger than that of FeCO, we might expect greater loss of nickel clusters compared with iron clusters. Unfortunately, we do not have any reliable rate coefficients for these reactions for $n > 0$.

Another factor to be considered is the direct or normal evaporation of small metal clusters, such as



If they evaporate too fast, clusters may not be able to form, hence reducing the possibility of SWNT production. In the present models the smallest metal cluster that produces SWNTs is that of Fe₁₀ or Ni₁₀. Therefore, clusters must grow to at least that size before SWNTs can be catalyzed. Several sets of rate coefficients are investigated for these evaporation reactions.

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Table I. Parameters used in Equation (5) for cluster evaporation rates.

Model	Surface tension, σ (N/m)	Ref. vapor pressure, P_{vref} (Pa)	E_v vapor (K)	Atom radius, r_1 (M)	Atom surface area, s_1 (m ²)
Girshick iron	1.7	6.83×10^{11}	47,400	1.40×10^{-10}	$2.46\text{E} - 19$
Girshick fit to Ni dimer bond	2.53 ^a	9.64×10^{11}	49,170	1.35×10^{-10}	$2.29\text{E} - 19$
Girshick fit to Fe dimer bond	3.65 ^a	6.83×10^{11}	47,400	1.40×10^{-10}	$2.46\text{E} - 19$

^aInferred by adjusting it in Eq. (5) to make E_a equal to the dimer bond energy.

In this study these possibilities were studied parametrically with the use of estimates of reaction rate coefficients based on limited knowledge of bond energies from the literature. The following discussion addresses the source of rate coefficients for various reactions in the models. These reactions are categorized as metal carbonyl dissociation and recombination reactions, dimer dissociation, and cluster evaporation (2), dimer nucleation, to some extent the exchange reactions (1), and the reaction



Other reactions in the model, such as cluster growth and CO attachment reactions, have been discussed in Ref. 3.

Cluster evaporation data for iron and nickel can be estimated using the formula of Rao et al.⁵ (denoted “Girshick” in this article). The expressions for cluster growth β_{ij} and evaporation E_i are, respectively,

$$\beta_{ij} = \left(\frac{3\nu_1}{4\pi} \right)^{1/6} \sqrt{\frac{6kT}{\rho_p} \left(\frac{1}{i} + \frac{1}{j} \right)} (i^{1/3} + j^{1/3})^2 \quad (4)$$

$$E_i = \beta_{1, i-1} n_s \exp(\Theta [j^{2/3} - (j-1)^{2/3}]) \quad (5)$$

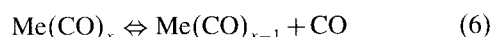
where $\Theta = \sigma s_1 / kT$ is the dimensionless surface energy, and ν_1 is the hard-sphere collision frequency of monomers, ρ_p is the density of bulk iron, i and j are the numbers of atoms in the colliding clusters, σ is the surface tension of the bulk metal, s_1 is the surface area of the monomer (atom), k is the Boltzmann constant, and T is the temperature. The saturation number density n_s is a function of temperature determined from a Clausius-Claperon-type relation, $p_s = p_{\text{vref}} \exp(-E_v/kT)$, where p_{vref} is a reference pressure and E_v is the energy required to remove an atom from the surface of the bulk substance. In the present study the saturation vapor pressure was determined by curve fits to the data of Ref. 6. Table I gives the parameters that were used in (4) and (5).

2. RESULTS

There are two sets of comparisons that were considered in comparing the influence of various reactions on the predicted growth of nanotubes. One is for iron and the other

for a “cooked-up” model of nickel. The basic rate coefficients for the model are those of the Ames 2001 version,⁷ which were based on values reported by Krestinin et al.⁸ and calculations of rate coefficients for $\text{Fe}(\text{CO})_x$ decomposition from bond energies by Sunderlin et al.¹ The basic differences in these iron and nickel models are the rate coefficients for carbonyl reactions and the metal cluster growth and evaporation reactions. The basic model is a variation of that described in Ref. 7, in which the iron clusters Fe_n and their corresponding Fe_nCO and CNT_n clusters are lumped into groups with 8, 16, 32, 64, . . . , 2048 iron atoms. Thus this model accounts for the agglomeration of clusters. Variations in the reaction rates that were assessed are those mentioned in the previous section. Definitions of these reactions and rate coefficient sources are given in the following paragraph.

Carbonyl rates are defined by those reactions of the form



For iron, these rates were determined by Ames Research Center from the bond energies of Sunderlin et al.³ For nickel, the rates were determined by simple substitution of the bond energy into their Arrhenius expressions for iron. No attempt was made to adjust the pre-exponential factors.

For both the iron and nickel models the reaction $\text{MeCO} + \text{MeCO} \Rightarrow \text{Me}_2 + 2\text{CO}$ was taken from Krestinin’s⁸ original set of reactions with its rate coefficient for iron. This reaction is usually negligible. It has an influence on the results only when there is no other mechanism for forming Me_2 .

The MeCO bond energy exhibits its greatest influence over dissociation. Two estimates were compared, one taken for the value of iron and the other for the value of nickel, 23.9 kJ/mol (2875 K Ames) and 170 kJ/mol (20,433 K), based on Sunderlin’s data.

Dissociation of metal dimers has a small influence on the results. The Krestinin⁸ value of the rate coefficient was used. These results and those of an estimate based on Girshick’s evaporation expression (5) were compared for iron. The surface tension in that expression was adjusted until the activation energy matched that of the bond energy for the iron dimer, 75 kJ/mol (or 9047 K).⁹ For nickel, the

rate coefficient for iron was used, except that the dissociation energy for Ni_2 was substituted in the Arrhenius energy term. The other method used expression (5) with the values for nickel substituted, and the Ni–Ni bond energy 203 kJ/mol (or 24,476 K).

Three models of evaporation of iron atoms from clusters were used. The first was the original set from Krestinin et al. for iron. The second was based on (5), with the rates determined from the surface energy of Ref. 4, and the third was based on adjustment of the surface energy until the activation energy for the dimer equaled the bond energy of 75 kJ/mol (9047 K). For nickel, three variations were studied: Krestinin⁸ values corresponding to iron, the Ref. 4 Girshick values, and the Girshick value calculated from (5) for nickel property data of a bond energy of 203 kJ/mol (24,476 K) and its vapor pressure. Figure 1 gives the evaporation rate coefficients for each model, evaluated at 1300 K. There are three basic sources of rates: Krestinin et al.,⁸ the Rao/Girshick⁴ equation (5) evaluated using nominal properties of Fe, and Eq. (5), with the surface tension adjusted so that the activation energy in the Arrhenius expression for dimer dissociation equals the value given in Ref. 9.

The conditions of this study are for a constant temperature of 1300 K and a pressure of 30 atmospheres, arbitrarily run for 0.1 s, a time on the same order as the duration of the flow in the reactor. (The actual flow time depends on the particular reactor tube diameter and length. These dimensions varied from one configuration to

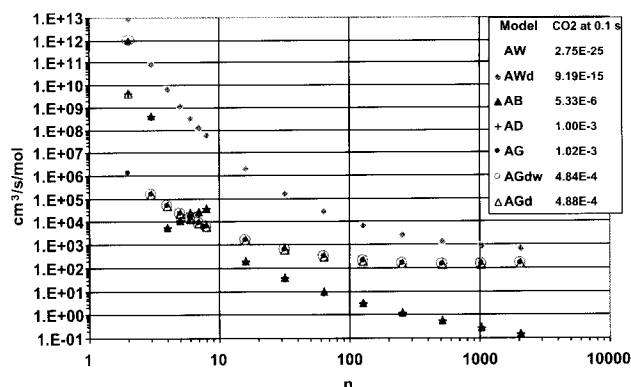


Fig. 1. Comparison of iron cluster reaction rate coefficients at 1300 K for clusters of size n for various cluster models. Also shown is the production of CO_2 as a measure of nanotube formation for each model.

another during development of the process.) The amount (mole fraction) of carbon dioxide produced at the end of this time was a measure of the effectiveness of the model. The starting amount of iron pentacarbonyl was 17 ppm in carbon monoxide. The basic cluster model is called the Binary 2048 model. Metal clusters have 1–8, 16, 32, 64, 128, 256, 512, 1024, and 2048 atoms. In this model there is a smaller number of species so that the cases run very fast. The chemical rate equations were solved with the program SENKIN of the CHEMKIN 3.61 package. The results of a set of calculations are presented in Tables II and III for iron and nickel, respectively.

Table II. Production of SWNTs with iron catalyst as indicated by the CO_2 mole fraction for ten combinations of rate coefficients and dimer nucleation.

Fe cluster model			$T = 1300 \text{ K}$			$P = 30 \text{ atm}$	
Desig.	Carbonyl rates	$\text{FeCO} + \text{Fe}_n$	Fe_2 dissoci.	Fe_n evap. $8 > n > 2$	Fe_n evap. $n = 8$	Relative CO_2 produced at 0.1 s, no Fe-Fe nucleation	Relative CO_2 produced at 0.1 s, Fe-Fe nucleation 4E15
AGd	Ames	Yes	Krestinin $E_a = 134 \text{ kJ/mol}$	Girshick	Girshick	1.00E+00	4.61E-01
AG	Ames	Yes	Girshick	Girshick	Girshick	1.00E+00	4.65E-01
AGdw	Ames	Yes	Ames $E_a = 75.2 \text{ kJ/mol}$	Girshick	Girshick	1.78E-02	9.71E-01
AD	Ames	Yes	Krestinin $E_a = 134 \text{ kJ/mol}$	Krestinin	Girshick	2.26E-02	9.52E-01
AB	Ames	Yes	Ames $E_a = 75.2 \text{ kJ/mol}$	Krestinin	Girshick	8.54E-05	5.08E-03
AW	Ames	Yes	Krestinin $E_a = 134 \text{ kJ/mol}$	Eq. (5) $w/E_a = 75.2 \text{ kJ/mol}$ bond	Eq. (5) $w/E_a = 75.2 \text{ kJ/mol}$ bond	1.49E-15	8.75E-12
AWd	Ames	Yes	Eq. (5) $w/E_a = 75.2 \text{ kJ/mol}$ bond	Eq. (5) $w/E_a = 75.2 \text{ kJ/mol}$ bond	Eq. (5) $w/E_a = 75.2 \text{ kJ/mol}$ bond	8.75E-24	2.62E-22
AGw	Ames	Yes	Eq. (5) $w/E_a = 75.2 \text{ kJ/mol}$ bond	Girshick	Girshick	n/a	3.90E-04
ANoX	Ames	No	Krestinin $E_a = 134 \text{ kJ/mol}$	Krestinin	Girshick	n/a	9.52E-01

Table III. Nickel catalyst production of SWNTs as indicated by the CO₂ mole fraction for ten combinations of rate coefficients and dimer nucleation.

Ni cluster model				T = 1300 K		P = 30 atm		Relative CO ₂ produced at 0.1 s, no Ni + Ni nucleation	Relative CO ₂ produced at 0.1 s, Ni + Ni nucleation 4E15
Case	Designation	Carbonyl Rates Ni(CO) _x x = 2, 4	NiCO + Ni _n	NiCO + NiCO	NiCO dissociation	Ni ₂ dissociation	Ni _n evaporation 8 > n > 2	Ni _n evaporation n > 8	
1	AWNiWOld-FeCO	Sunderlin	Yes	0	Ames Fe E _a = 24 kJ/mol	Ames from 203 kJ/mol bond	Girshick from 203 kJ/mol bond	Girshick from 203 kJ/mol bond	3.90E – 01
2	AWNiOldFeCO-NiCONiCO	Sunderlin	Yes	Krestinin Fe rate	Ames Fe E _a = 24 kJ/mol	Ames from 203 kJ/mol bond	Girshick from 203 kJ/mol bond	Girshick from 203 kJ/mol bond	3.90E – 01
3	AWNiS	Sunderlin	Yes	0	Sunderlin E _a = 170 kJ/mol	Ames from 203 kJ/mol bond	Girshick from 203 kJ/mol bond	Girshick from 203 kJ/mol bond	4.37E – 12
4	AGNiOldFe ₂	Sunderlin	Yes	0	Ames Fe E _a = 24 kJ/mol	Girshick from 203 kJ/mol bond	Girshick from 203 kJ/mol bond	Girshick from 203 kJ/mol bond	3.35E – 01
5	AGNoXNiNoNiNoNiCONiCO	Sunderlin	No	0	Ames Fe E _a = 24 kJ/mol	Ames Fe E _a = 134 kJ/mol	Girshick from 203 kJ/mol bond	Girshick from 203 kJ/mol bond	n/a
6	AWNi	Sunderlin	Yes	0	Sunderlin E _a = 170 kJ/mol	Girshick from 203 kJ/mol bond	Girshick from 203 kJ/mol bond	Girshick from 203 kJ/mol bond	8.07E – 22
7	ADNiOldFe ₂	Sunderlin	Yes	0	Ames Fe E _a = 24 kJ/mol	Ames Fe E _a = 134 kJ/mol	Girshick Fe	Girshick Fe	7.90E – 01
8	ADNi	Sunderlin	Yes	0	Sunderlin E _a = 170 kJ/mol	Ames Fe E _a = 134 kJ/mol	Ames Fe	Girshick Fe	9.67E – 17
9	ADNiCONiCO	Sunderlin	Yes	Ames Fe rate	Sunderlin E _a = 170 kJ/mol	Ames Fe E _a = 134 kJ/mol	Ames Fe	Girshick Fe	2.66E – 14
10	ADNoNuNoNiNoNiCONiCOx	Sunderlin	No	0	Sunderlin E _a = 170 kJ/mol	Ames Fe E _a = 134 kJ/mol	Ames Fe	Girshick Fe	n/a

2.1. Iron

The nominal iron case is denoted AD in Table II. All of the rates are based on the Ames model, except that evaporation of the large iron clusters was determined from (5), Girshick. This model produced a CO₂ mole fraction of 0.001 in 0.1 s. The production of CO₂ relative to the maximum case is given in the table for each variation of the model. Variations on this model using other values of Fe₂ dissociation and Girshick evaporation rates for small Fe clusters affected the results only slightly. Reducing the Fe-Fe nucleation rate to zero reduced production by almost two orders of magnitude for the nominal case, but increased CO₂ slightly in the other cases where Girshick evaporation rates were used along with a smaller bond energy of 75 kJ/mol. When the smaller bond energy is used along with Krestinin⁸ evaporation rates for small clusters, the amount of CO₂ is significantly reduced. It appears that evaporation takes its toll on cluster formation and hence on their ability to catalyze the Boudouard reaction. The situation is exacerbated when the evaporation of clusters is based on calculations of the rate coefficients using (5) and the 75-kJ/mol bond energy, especially when the dimer dissociation rate coefficient uses this bond energy in its Arrhenius coefficient.

To test the influence of the exchange of Fe from reactions with FeCO, they were deleted in the last case in Table II. There was a negligible effect on the results, indicating that these reactions are not important, except when the reaction $\text{Fe} + \text{Fe} \Rightarrow \text{Fe}_2$ was also deleted from the model. There needs to be at least one reaction for forming the dimer Fe₂.

2.2. Nickel

The models for nickel as a catalyst are based on more approximate estimates of the rate coefficients than the basic iron model. Probably the most representative nickel models are cases 3 and 6 in Table III. In those cases the rate coefficients have been modified to account for the bond energies associated with nickel. At 0.1 s the mole fraction of CO₂ produced in those two cases relative to the maximum case is 4.36×10^{-15} and 8.07×10^{-25} , respectively. This is negligible production and reflects the nature of the strong NiCO bond 170 kJ/mol (20,422 K). This strong bond prevents the formation of Ni clusters, thus inhibiting SWNT growth. The influence of the bond energy is demonstrated in cases 1, 2, 4, and 7, where the NiCO dissociation rate was made the same as for iron. In those cases the production of CO₂ is similar to that for the iron model. Behavior similar to that of iron is seen in the influence of Ni-Ni dimer formation. When a NiCO bond energy of 170 kJ/mol is used there is some influence in the NiCO + NiCO reaction and the NiCO + Ni_n exchange reactions, as seen in cases 6, 8, 9, and 10. These reactions are neglected in the models of Dateo et al.⁵

3. CONCLUSIONS

Simulations of reactions in the HiPco process for SWNT production were carried out to investigate the influence of various possible reactions in the scheme and the effect of bond energy differences between iron and nickel. Time-dependent calculations were made for a constant temperature of 1300 K and a pressure of 30 atmospheres, using a premixed reactor solution to the chemical rate equations. The principal metric for evaluating the models was the mole fraction of CO₂ produced by the Boudouard reaction, which is a measure of the total production of SWNTs.

It was found that the metal-CO bond energy has a major influence on the production of CO₂. The higher NiCO bond energy almost eliminates the production of CO₂, whereas the smaller bond energy of FeCO leads to significant production. Moreover, the rate of dimer dissociation and small cluster evaporation affects the production of CO₂ by limiting the rate of cluster growth and thus the number of clusters available to catalyze SWNT growth. This suggests that if CO reacts with metal clusters and removes atoms from them by forming MeCO, this has the effect of enhancing the evaporation rate and reducing SWNT production.

Because of the possibility of producing dimers via FeCO reactions, the rate of direct $\text{Fe} + \text{Fe} \Rightarrow \text{Fe}_2$ dimer formation did not have a big influence on CO₂ production. The same thing was observed for nickel if the bond energy of Ni-CO was assumed to be equal to that of iron, a nonrealistic circumstance.

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